Electrochemical and
Solid-State Letters

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To cite this article: William G. America and S. V. Babu 2004 *Electrochem. Solid-State Lett.* **7** G327

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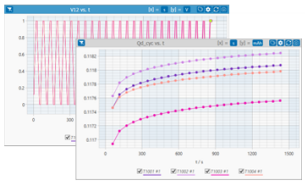

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Electrochemical and Solid-State Letters, **7** (12) G327-G330 (2004)
1099-0062/2004/7(12)/G327/4/$7.00 © The Electrochemical Society, Inc.

Slurry Additive Effects on the Suppression of Silicon Nitride Removal during CMP

William G. America[a,*] and S. V. Babu[b,*,z]

[a]*IBM Microelectronics, Hopewell Junction, New York 12533, USA*
[b]*Department of Chemical Engineering and Center for Advanced Materials Processing, Clarkson University, Potsdam, New York 13699, USA*

The removal of silicon nitride during chemical mechanical planarization (CMP) of shallow trench isolation structures occurs through tribological wear-induced conversion of the nitride to an oxide. Hence, silicon nitride removal rate can be drastically reduced if appropriate chemicals that can inhibit this conversion at the surface are added to the CMP slurry. This paper presents data on the effects of numerous amino acids and other chemical additives with ceria abrasives on the removal rate of silicon nitride during CMP. A mechanism is presented that explains the suppression of nitride removal during CMP, observed only with some of the amino acids and proline in particular.
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Manuscript submitted April 30, 2004; revised manuscript received July 10, 2004. Available electronically November 1, 2004.

Shallow trench isolation (STI) has become the preferred complimentary metal oxide semiconductor (CMOS) isolation process technology[1,2] because feature size can be made very small, allowing higher device density compared to local oxidation of silicon (LOCOS) isolation techniques. STI processes involve etching a trench through a thin layer of silicon nitride lying over a thin silicon oxide film and into the underlying epi-silicon. A silicon oxide layer is subsequently deposited over the entire wafer, overfilling the trenches. This oxide layer is deposited typically by a plasma-enhanced chemical vapor deposition (PECVD) process using tetraethylortho silicate (TEOS) as the source of silicon. Chemical mechanical planarization (CMP) is used to remove excess TEOS oxide, stopping on or in the nitride layer.

As STI technology matured, several CMP slurries used to planarize the CVD or TEOS oxide filled trench have become commercially available.[3-6] These slurries offer improved selectivity for planarizing the trench fill material while keeping the polish stop layer (the nitride film) uniform. During CMP, achieving a high polish rate selectivity of PECVD silicon oxide to silicon nitride is important, while simultaneously suppressing the nitride removal rate to a very low value (a few nm/min or less). Removal rates of trench fill material can be made high by combining high polishing pressure and pad velocity with very abrasive slurry particles. However, the nitride removal rate will also be high under such conditions and the final remaining nitride layer thickness nonuniformity can be a significant issue.

A preferred STI process can be achieved by driving the removal rate of the protective nitride layer as low as practical while maintaining a reasonable rate for the fill oxide. Additionally, by suppressing the nitride removal rate, issues associated with pattern dependent nonuniformity with CMP can be reduced or minimized. However, when the high selectivity is coupled with a very low nitride removal rate, dishing of the trench oxide may become excessive resulting in severe topographic differences after nitride removal. Balancing these factors and determining which variables are important to control will lead to a good STI process.

Experimental

All CMP experiments were carried out on either a Strasbaugh 6DS-SP or a Westech 372 CMP tool. Wafer polishing was done with an applied down force of 5 psi, a spindle speed of 50 rpm, and a pad velocity of 75 cm/s. The investigation of the influence of the addition of several different amino acids and other additives on the removal rate of silicon nitride during CMP was carried out using a Ferro SRS 521 ceria slurry with a Rodel IC1400 pad. The primary amino acids investigated were glycine, proline, alanine, lysine, and arginine. Derivatized amino acids, N-methyl and N,N-dimethylglycine, along with 3-aminobutyric acid, picolinic and iso-nicotinic acids were also used as additives in the ceria slurry. All are shown in Fig. 1.

Each slurry was prepared with 1 wt % ceria and 2 wt % additive in DI water. The slurry was adjusted to pH 9.6 $\pm$ 0.1 with 1 N KOH solution. During the polishing experiments, the ceria slurry was stirred continuously to prevent settling of the abrasive. The slurry was delivered to the pad center at 150 mL/min. The pad was conditioned initially and again after each wafer was polished to ensure a consistent pad surface condition. After CMP, all wafers were immediately rinsed with DI water to remove any abrasive and additive and dried with nitrogen. The pre- and post-polishing thicknesses of the silicon oxide and silicon nitride films were obtained using either a Tencor TF-1 or a Filmetrics Model F-20 and were used to determine the film removal rate. Each polishing experiment was conducted for 3 min and the experiment repeated three times and the rates were averaged.

Results

The CMP removal rates and selectivities for silicon nitride and TEOS oxide films are shown in Table I. The greatest suppression of the silicon nitride removal rate occurs with lysine, arginine, and proline and less with N-methylglycine, glycine and alanine. Little or no nitride suppression occurs using amino acids N,N-dimethylglycine and 3-aminobutyric acid and with the pyridines, picolinic and iso-nicotinic acid. Except for lysine and arginine, the TEOS oxide polish rate for all the other additives remains unaffected at about 430-460 nm/min. The TEOS-silicon nitride removal rate selectivities ranged from as low as ~6:1 for 3-aminobutyric acid to 228:1 for proline.

All ten slurry additives investigated here have a carboxylic acid group. However, only those with an amino group having at least one hydrogen exhibit high selectivity. Also, while the amine hydrogen is necessary it is apparently not sufficient, as 3-aminobutyric acid exhibits no effect on silicon nitride rate. Unlike the others, 3-aminobutyric acid does not have the amino group in the alpha position with respect to the carboxylic acid, indicating a strong spatial requirement between the carboxylic acid and the amino group with respect to the silicon nitride surface. It appears that the amino group must be attached to the first carbon (alpha position) adjacent to the carboxylic acid. This strongly suggests that hydrogen bonding may play a role in suppressing silicon nitride removal rate during CMP.

Arginine and lysine have the strongest effect on silicon nitride removal rate, but they also strongly suppress TEOS removal rate, which is unacceptable. Both glycine and N-methylglycine are similar in their behavior, with N-methylglycine slightly more effective at suppressing the silicon nitride removal rate. The methyl group does not hinder the interaction of amine hydrogen with the silicon nitride

* Electrochemical Society Active Member.
z E-mail: babu@clarkson.edu

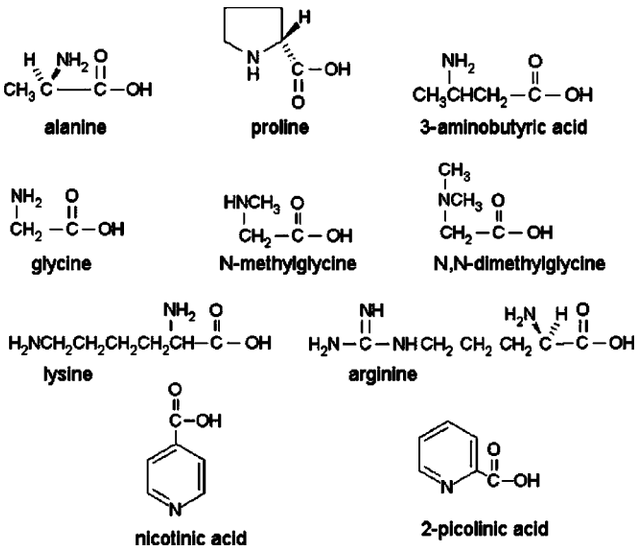

Figure 1. Structures of additives used to modify the silicon nitride removal rate.

surface and may actually increase the hydrogen bond strength. Proline, with a single amino hydrogen, has a very low silicon nitride polishing rate, similar to arginine and lysine, but does not reduce the TEOS removal rate. Thus, proline-ceria slurry has the highest TEOS to silicon nitride removal rate selectivity of all the additives studied.[7]

Discussion

A CMP removal mechanism for silicon nitride by an aqueous abrasive slurry has been proposed earlier[8,9] and is based on the rate limiting role played by the slow hydrolysis of silicon nitride. Even though the hydrolysis itself is thermodynamically favorable ($\Delta G_{298} = -147$ kcal/mol) with the net reaction[10,11]

$$Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3 \qquad [1]$$

the conversion rate is low. At low temperatures, typical thickness of the resulting silicon oxide layer is only about 1-2 nm. This oxide film, according to Hu *et al.*,[8,9] is removed during CMP. The conversion process can be enhanced through tribological wear[12] that occurs during CMP. It was suggested that the abrasives act as points of wear, enhancing the hydrolysis of the silicon nitride and subsequently removing the freshly formed silicon oxide surface.

Hence, our results suggest that adding arginine, lysine, or proline to the slurry reduces or nearly eliminates the conversion of the silicon nitride surface and prevents the formation of the silicon oxide layer by adsorbing onto the nitride surface. Adsorption of proline on the ceria particles used in the slurry does not appear to occur.[13] Such an interaction of the slurry additive with the silicon nitride surface must be through the nitrogen of the oxide-free silicon nitride layer which is exposed after the top 1-2 nm of silicon oxide layer is removed. The structure of the additive and its interaction with the silicon nitride surface determine to what extent subsequent conversion of the silicon nitride occurs.

Carboxylic acid groups appear to be necessary to suppress hydrolysis but are not sufficient as shown by the unaffected silicon nitride removal rates with iso-nicotinic and picolinic acid-ceria slurries. Inhibition of the hydrolysis and the suppressed CMP removal of silicon nitride requires hydrogen bonding and a carboxylic acid group. A further requirement appears to be that the hydrogen bonding group is in the alpha position with respect to the carboxylic acid, as suggested by the unaffected silicon nitride CMP rate with 3-aminobutyric acid as the slurry additive. In this case, the amino group is displaced one carbon atom, defining spatial requirement for optimal interaction of the additive's functional groups with the silicon nitride surface. The essential role played by this hydrogen bonding is confirmed by the inability of the additives lacking an amino hydrogen, N,N-dimethylglycine, iso-nicotinic, and picolinic acid, to suppress silicon nitride removal.

The negligible removal rate of nitride with arginine, lysine, and glycine suggests that the association of the additive with the silicon nitride surface is very fast relative to tribological wear induced oxidation. The influence of arginine and lysine also extends to the suppression of silicon oxide removal rate. These two amino acids are different from the others used in the experiments. Both possess a side chain containing additional amino groups which protonate when the pH $<$ pI (10 and 11 for lysine and arginine, respectively[14,15]). At ~pH 9, where the polishing experiments were performed, the positively charged arginine and lysine are attracted to the negatively charged silanol groups on the silicon dioxide film. This results in their adsorption and subsequent suppression of the silicon dioxide removal. Such an adsorption of these two basic amino acids (arginine, lysine) on negatively charged sand surfaces has been reported in the literature.[16,17] All the other amino acids with pI's of ~6-7[14,15] will be negatively charged (pH $>$ pI) and will not adsorb on the silicon dioxide surface.

Table I. Silicon oxide and silicon nitride removal rates for slurries with different amino acid additives. All rates are at pH 9.6±0.1. Selectivity=oxide rate/nitride rate.

Amino acid	Nitride rate (nm/min)	Oxide rate (mn/min)	Selectivity
Arginine	1	23	23
Lysine	1	71	71
Proline	2	456	228
N-methylglycine	12	467	38.9
Alanine	18	455	30.3
Glycine	18	435	24.2
Picolinic acid	65	423	6.5
N,*N*-dimethylglycine	68	438	6.4
3-Aminobutyric acid	72	442	6.1
Isonicotinic acid	71	441	6.2

Proline–Nitride Surface Interaction

Suppression of silicon nitride removal can be investigated further by examining the three dimensional structure of silicon nitride films. Bond length of Si-N (1.74 Å), and lengths and angles of N-Si-N (2.84 Å and 120°) Si-N-Si (3.01 Å and 109.4°) in the silicon nitride unit cell have been already reported.[18] These dimensions are consistent with the β-silicon nitride structure, with the unit cell shown in Fig. 2 and as reported by Loong *et al.* using X-ray diffraction patterns (XRD) on CVD silicon nitride films.[19,20] The measured distances and angles between critical atoms and the calculated critical distance were used to determine how proline would interact spatially with the silicon nitride surface.

Proline can interact with the silicon nitride surface both through the O^- atoms of the carboxylic acid group and through hydrogen bonding of the amino hydrogen (see Fig. 3). The proline O^- atoms can interact with the silicon atoms similar to the interactions of carboxylic oxygen atoms with titania and zinc oxide.[21-23] Formic acid, glycine, and bis-isonicotinic acid bind through a bidentate bridging of the two carboxylic O^- atoms to two titanium or zinc atoms[21-23] in these cases. The oxygen atoms that straddle the silicon nitride cell are attached to a cross-cell pair of silicon atoms with the remainder of proline tilted over the silicon nitride unit cell. The calculated distance, d_c, from mid-way between the two silicon atoms to the nitrogen is 3.12 Å. The distance from midway between the two oxygen atoms of proline to the amino hydrogen is 2.86 Å. If a 10° tilt, found with formic acid-titania, is used for Si-O-C of the proline-nitride adsorption also, then the proline amino hydrogen is displaced an additional 0.10 Å over the nitrogen of the silicon ni-

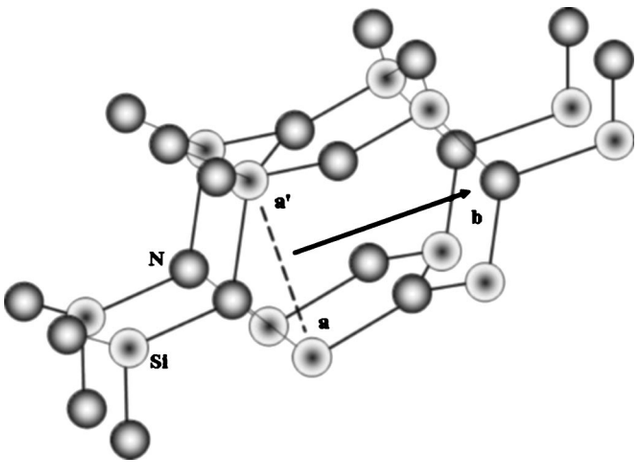

Figure 2. Beta-silicon nitride unit cell (top view, parallel to the screen). Critical distance, d_c, is from the middle of the distance between the silicon atoms (a,a′) to a nitrogen atom (b) that could overlap effectively with the carboxylic atoms and the amine hydrogen, respectively. Some covalent bonds of some Si and N atoms are not shown.

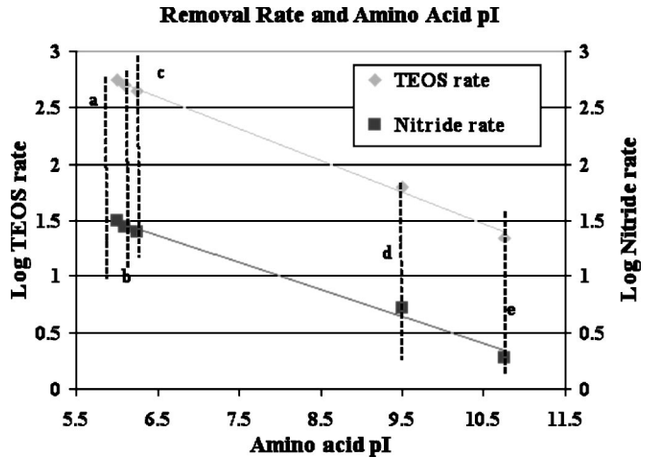

Figure 4. CMP removal rate of silicon nitride (lower) and silicon oxide (top) as a function of the amino acid pI. The amino acids are (a) glycine, (b) alanine, (c) proline, (d) lysine, and (e) arginine. Both the silicon nitride and silicon oxide removal are suppressed by the amino acids arginine and lysine. The two dashed lines are linear fits to the data.

tride. This results in a lateral difference of less than 0.16 Å between the distance of Si to N and O to H atoms. Moreover, it places the proline amino hydrogen almost directly over the nitrogen of the silicon nitride unit cell as shown in Fig. 3.

Molecular modeling also shows the same proline-nitride fit. The hydrogen bonding distance is 2.2 Å with an O-Si bond distance of 1.68 Å at the energy minimum. This close proximity shows that hydrogen bonding is an integral part of the suppression mechanism. The interaction of the carboxylic acid oxygen with the silicon and the hydrogen bonding with the nitrogen (Fig. 3) are consistent with the observed role of the additives to the ceria slurry. These interactions are required and appear to be sufficient to inhibit the nitride hydrolysis and conversion of the silicon nitride surface.

Role of pH

The influence of pH is also critical for the suppression of the nitride removal rate and its effect with the proline-ceria slurry was presented earlier[6,7] and not repeated here. In brief, the lowest nitride removal rate was at pH 9.7.[6,7] Silicon nitride removal over the pH range of 6 to 8 occurs at an essentially constant rate, and as the slurry pH exceeds 8, silicon nitride removal rate decreases to a minimum at pH 9.7. As pH increases further, the silicon nitride removal rate increases by nearly 10 times at pH 11.

This behavior can be explained through the surface charge present on silicon nitride when devoid of an oxide layer. Surface silicon oxide on silicon nitride can be stripped off by an acid or a base leaving a native silicon nitride surface.[24] The isoelectric point (IEP) of this oxide-free silicon nitride was shown to be 9.7,[24] exactly where the minimum in the removal rate of silicon nitride occurs. Thus it appears that this minimum in the nitride removal rate is related to the surface having near zero net charge, which presumably leads to the optimal association of proline with the nitride surface.

Further influence of charge interactions between the additives and the silicon nitride surface can be found through the amino acid ionization levels. The extent of the ionization, pI, of the amino acids[14,15] is defined by

$$\mathrm{pI} = 1/2(\mathrm{pk_{a1}} + \mathrm{pk_{b1}} - \mathrm{pk_w}) \qquad [2]$$

where pK_{a1}, pK_{b1}, and pK_w are the acid, base, and water dissociation constants, respectively. The removal rates of silicon nitride and silicon oxide for several amino acids are shown in Fig. 4 as a function of pI. As pI increases the removal rates for both silicon nitride and silicon oxide decrease linearly.

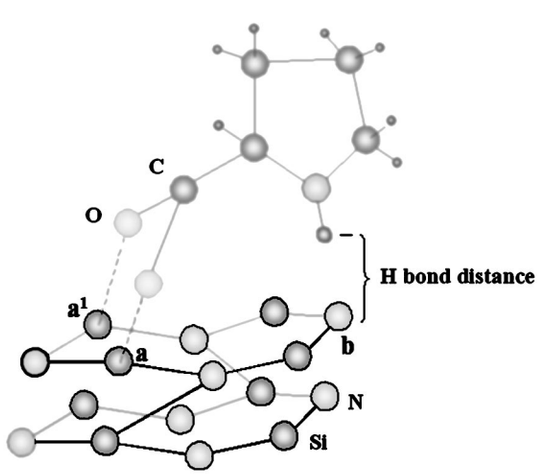

Figure 3. Schematic representation of proline on silicon nitride (side view of the unit cell of Fig. 2). The carboxylic acid bridges the silicon atoms of silicon nitride resulting in a bidentate bridge. The amine hydrogen lies nearly overhead of a silicon nitride nitrogen atom making hydrogen bonding possible. Some covalent bonds of all the Si and N atoms are not shown.

Conclusion

Selective removal of silicon nitride with amino acid additives in ceria slurries results from suppression of the hydrolysis and exposure of the base silicon nitride film. After the silicon oxide is removed during CMP in an alkaline slurry, the proline adsorbs onto the nitride surface through a combination of hydrogen bonding and coupling of oxygen atoms of the carboxylic acid group with an adjacent pair of silicon atoms of the silicon nitride surface. The interaction of the additive with the silicon nitride surface is sufficiently strong to inhibit tribological wear from a slurry abrasive on the silicon nitride and yet have little or no effect on the removal rate of TEOS based silicon oxides. Finally, the surface charge of the silicon nitride has a strong influence on its hydrolysis and on the CMP removal rate.

Clarkson University assisted in meeting the publication costs of this article.

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